

# Sodium Promotion of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts Operated under Simulated “Three-Way” Conditions

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**Sodium promotion strongly enhances the performance of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts operated under simulated “three-way” conditions over a range of stoichiometry from fuel rich to fuel lean. The optimally promoted catalyst (7.0% w/w Na) exhibits a  $\sim$ 50°C lower light-off temperature than the unpromoted sample when tested under stoichiometric feed conditions. Sodium promotion is also beneficial under both oxidising and reducing conditions. Under reducing conditions the alkali prevents poisoning by hydrocarbon deposits, therefore maintaining high NO conversions. Under oxidising conditions sodium significantly reduces the formation of N<sub>2</sub>O (nitrogen selectivity,  $S_{N_2} = 80\%$  over the optimally promoted sample compared to  $\sim$ 45% over the unpromoted catalyst at 325°C). The improvement in activity and selectivity is understandable in terms of Na-induced changes in the adsorption strength of the various reactants on the Pd surface, accompanied by enhanced NO dissociation.** © 2001 Academic Press

**Key Words:** NO; palladium; simulated exhaust gas; promotion; sodium; N<sub>2</sub>O; selectivity; fuel rich; fuel lean.

## 1. INTRODUCTION

Automotive three-way catalytic converters employ various combinations of Pt, Pd, and Rh for the simultaneous removal of NO<sub>x</sub>, CO, and unburned hydrocarbons (1). Of these metals, rhodium is the key component in relation to NO<sub>x</sub> reduction because of its high activity for the dissociative chemisorption of NO (2). However, due to the scarcity of this metal and its subsequent high cost, much attention has recently been devoted to strategies for reducing and/or replacing the usage of rhodium in three-way catalysis (TWC).

A number of studies have focussed on promoting NO reduction over Pd by doping the support material with additives such as La<sub>2</sub>O<sub>3</sub> (3, 4), BaO (4, 5), or MoO<sub>3</sub> (6–8), or by using supports other than alumina, such as yttria-stabilised zirconia (9). Muraki *et al.* (3) found that NO reduction over palladium catalysts was significantly reduced under fuel-

rich conditions due to self-poisoning by hydrocarbon. This poisoning effect was diminished on addition of La<sub>2</sub>O<sub>3</sub> to the catalyst, and was attributed by the authors to an electronic interaction between basic lanthana and Pd, resulting in a decrease in the binding strength of the adsorbed hydrocarbon species on the palladium surface. Similar effects were observed by Shinjoh *et al.* in the case of Ba (and Sr)-containing catalysts (4, 5).

Halasz *et al.* (6, 7) investigated the reduction of NO by CO, H<sub>2</sub>, and CO + H<sub>2</sub> mixtures over Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd-MoO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts both in the presence and in the absence of oxygen. Under slightly oxidising conditions and temperatures between 300°C and 550°C, it was observed that MoO<sub>3</sub>-containing catalysts were more active for the reduction of NO to N<sub>2</sub> and N<sub>2</sub>O. This effect was again attributed to an interaction between palladium and the supported oxide.

Electrochemical promotion (EP) (10) has recently been used to investigate the influence of alkali on the reactions of NO + CO (11) and NO + C<sub>3</sub>H<sub>6</sub> (12) over platinum. It was shown that sodium, electrochemically supplied to the metal surface, strongly influenced its catalytic properties resulting in large increases in both activity and N<sub>2</sub> selectivity. Guided by these EP studies, Yentekakis *et al.* (13, 14) and Macleod *et al.* (15) investigated the influence of sodium addition to conventional dispersed palladium (13), platinum (14), and rhodium (15) catalysts for the reduction of NO by propene. In each case large increases in both activity and N<sub>2</sub> selectivity were observed. For palladium supported on yttria-stabilised zirconia (13), rate increases by over an order of magnitude were observed on addition of sodium, accompanied by increases in nitrogen selectivity from 75% over the unpromoted catalyst to >95% over the optimally promoted catalyst.

Recently we investigated the influence of sodium on Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts tested under simulated TWC conditions at the stoichiometric point (16). Under the conditions employed very strong promotional effects were observed in relation to both the light-off temperature and N<sub>2</sub> selectivity. Here, in a related study which also extends the range of conditions explored, we report on the promotional effect

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of Na addition to Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> operated in simulated TWC exhaust gas under stoichiometric, lean, and rich conditions. The optimally promoted catalyst (7.0% w/w Na) exhibited a  $\sim 50^\circ\text{C}$  lower light-off temperature than the unpromoted sample when tested under stoichiometric feed conditions. Sodium promotion was also found to be beneficial under oxidising and reducing conditions, maintaining high NO conversions under fuel-rich conditions and significantly reducing the formation of N<sub>2</sub>O under oxidising conditions.

## 2. METHODS

### 2.1. Materials

The 0.5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst which formed the basis of this study was prepared by impregnation of an alumina carrier (Aldrich, SA = 100 m<sup>2</sup> g<sup>-1</sup>) with an aqueous solution of palladium(II) nitrate. Batches of this precursor were subsequently impregnated with solutions containing various concentrations of sodium nitrate. The solution concentrations were chosen so as to yield a range of sodium loadings from 0 to 12 wt%. Following impregnation the catalysts were dried in air for 4 h at 110°C and subsequently crushed/sieved to yield grain sizes in the range 255–350  $\mu\text{m}$ . Metal dispersions were determined using the CO methanation technique (17, 18). Prior to this measurement the samples (100 mg) were calcined in air (60 cm<sup>3</sup> min<sup>-1</sup>) for 6 h at 500°C followed by reduction in H<sub>2</sub> (60 cm<sup>3</sup> min<sup>-1</sup>) for 1 h at 250°C. A summary of the relevant data can be found in Table 1.

### 2.2. Light-Off Performance and Influence of Feed Composition

Catalyst testing was performed using a quartz tubular reactor (4 mm i.d.). During light-off measurements the catalyst sample (75 mg) was retained between plugs of quartz wool, with a K-type thermocouple placed in the centre of the bed. Reactant gases (MG Gas Products) were delivered by a series of independent mass flow controllers (MKS Instruments). The feed composition employed

during light-off testing was as follows: 1000 ppm NO, 1067 ppm C<sub>3</sub>H<sub>6</sub>, 7000 ppm CO, and 7800 ppm O<sub>2</sub> diluted in ultrapure He. The total flow was 300 cm<sup>3</sup> min<sup>-1</sup> corresponding to a reciprocal weight time velocity  $W/F = 0.015 \text{ g s cm}^{-3}$ . Prior to testing the samples were calcined in air (60 cm<sup>3</sup> min<sup>-1</sup>) for 6 h at 500°C.

The stoichiometric number,  $S$ , used to characterise the simulated exhaust gas mixture is defined as

$$S = \frac{2[\text{O}_2] + [\text{NO}]}{[\text{CO}] + 9[\text{C}_3\text{H}_6]}$$

The above values of reactant feed composition correspond to  $S = 1$ . The influence of feed composition on reactant conversions and nitrogen selectivity has also been investigated in the range  $0.90 \leq S \leq 1.10$ . These experiments were carried out by maintaining the catalyst bed at a constant temperature (325°C) whilst varying the oxygen concentration between 6970 ppm ( $S = 0.90$ ) and 8630 ppm ( $S = 1.10$ ). A number of experiments performed by varying CO and C<sub>3</sub>H<sub>6</sub> concentrations were found to produce identical results.

The reactor outflow was analysed using a combination of the following techniques: gas chromatography (Shimadzu 14B with TCD detector), chemiluminescence (Signal 4000 series NO/NO<sub>2</sub> detector) and nondispersive infrared (two dual-channel Siemens Ultramat 6 analysers calibrated for CO/CO<sub>2</sub> and NO/N<sub>2</sub>O). A Poropak N column was employed for the chromatographic separation of CO<sub>2</sub>, N<sub>2</sub>O, and C<sub>3</sub>H<sub>6</sub>, and a molecular sieve 5A column was used for the separation of N<sub>2</sub>, O<sub>2</sub>, and CO. The carbon and nitrogen mass balances (based on C<sub>3</sub>H<sub>6</sub>, CO, CO<sub>2</sub>, NO, N<sub>2</sub>, N<sub>2</sub>O, and NO<sub>2</sub>) were found to close within 1% and 2%, respectively.

## 3. RESULTS

### 3.1. Catalyst Characterisation

Active metal areas were determined by the CO methanation technique, after calcination in air at 500°C and reduction in hydrogen for 1 h at 250°C. This technique (18) makes use of a sensitive FID detector to monitor the conversion of chemisorbed CO to methane on metal sites. Prereduction was necessary in order to generate fully reduced metal sites. The results obtained are shown in Table 1. Metal dispersion was calculated assuming a 1 : 1 CO to surface metal atom ratio. Moderate alkali loadings resulted in a slight increase in metal dispersion (similar to the effects observed by Rieck and Bell (19) on alkali-doped Pd/SiO<sub>2</sub> catalysts) from  $\sim 47\%$  for the unpromoted catalyst to 54% for the 3.5% Na sample. However, increasing further the alkali loading to 7.0 wt% or above resulted in a significant decrease in apparent dispersion, which we attribute to site blocking by surface sodium compounds. Indeed, the 12.0 wt% Na sample was found to have very low activity for all the reactions investigated due to this site blocking effect.

TABLE 1

Properties of 0.5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts<sup>a</sup>

Na loading (wt%)	CO uptake ( $\mu\text{mol/g}$ )	Dispersion (%)
0	21.98	46.8
1.8	23.49	49.9
3.5	25.34	54.0
7.0	17.67	37.5
12.0	5.32	11.3

<sup>a</sup> Calcined in air for 6 h at 500°C and reduced in H<sub>2</sub> for 1 h at 250°C prior to measurement.

TABLE 2

Light-Off Temperatures ( $T_{50}$  for CO, C<sub>3</sub>H<sub>6</sub>, and NO) and Maximum N<sub>2</sub>O Formation for the Various Catalysts

Na loading (Wt%)	$T_{50}$ (°C)			Max NO conv to N <sub>2</sub> O (%)	Temp for max N <sub>2</sub> O (°C)
	CO	C <sub>3</sub> H <sub>6</sub>	NO		
0	303	309	316	17	320
3.5	255	267	275	31	280
7.0	255	274	278	21	283

### 3.2. Effect of Sodium Loading on Light-Off Performance

In the following discussion the light-off temperature,  $T_{50}$ , is defined as the temperature required to obtain 50% conversion of a particular reactant. The values for CO, C<sub>3</sub>H<sub>6</sub>, and NO conversion over the various catalysts are listed in Table 2. Also listed are the peak maximum values for N<sub>2</sub>O formation along with the temperature at which this maximum occurs.

Figure 1 depicts the influence of sodium loading on CO conversion as a function of temperature under stoichiometric conditions (1000 ppm NO, 7000 ppm CO, 1067 ppm C<sub>3</sub>H<sub>6</sub>, and 7800 ppm O<sub>2</sub>,  $W/F=0.015$  g s cm<sup>-3</sup>). It is apparent from these data that Na exerts a pronounced effect, with the light-off temperature decreasing from ~303°C over the unpromoted 0% Na sample to ~255°C over both 3.5 and 7.0 wt% Na-containing samples.

The corresponding data for propene conversion are displayed in Fig. 2. Again, a significant decrease in light-off temperature is observed on addition of sodium, from 309°C over the sodium-free sample to 267°C for 3.5 wt% Na and 274°C for 7.0 wt% Na. Similar effects were observed in the case of NO conversion as shown in Fig. 3. In this case the

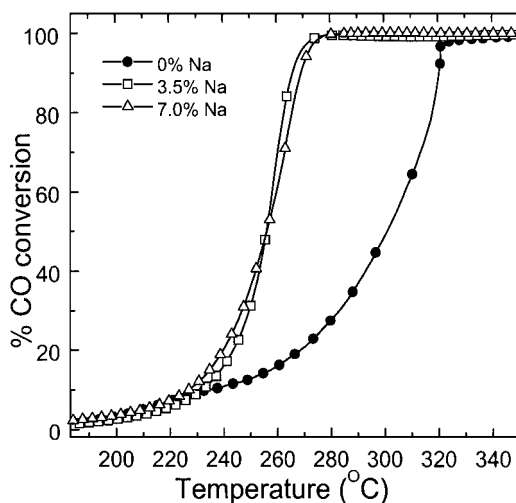


FIG. 1. The influence of sodium content on light-off performance for CO oxidation.  $S=1$ , [NO]=1000 ppm, [C<sub>3</sub>H<sub>6</sub>]=1067 ppm, [CO]=7000 ppm, [O<sub>2</sub>]=7800 ppm,  $W/F=0.015$  g s cm<sup>-3</sup>.

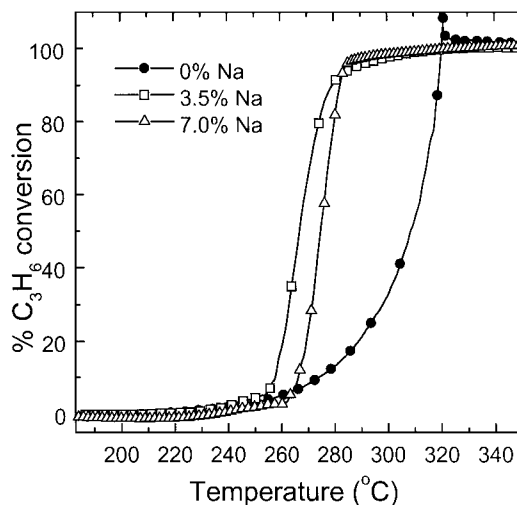


FIG. 2. The influence of sodium content on light-off performance for C<sub>3</sub>H<sub>6</sub> oxidation.  $S=1$ , [NO]=1000 ppm, [C<sub>3</sub>H<sub>6</sub>]=1067 ppm, [CO]=7000 ppm, [O<sub>2</sub>]=7800 ppm,  $W/F=0.015$  g s cm<sup>-3</sup>.

decrease in light-off temperature was from approximately 316°C over the unpromoted sample to ~275°C for both 3.5 and 7.0 wt% Na samples.

The influence of Na on N<sub>2</sub>O formation and the corresponding nitrogen selectivity are depicted in Fig. 4. Here the nitrogen selectivity is defined as

$$\%S_{N_2} = \frac{[N_2]}{([N_2] + [N_2O])} \times 100/1.$$

It is clear from Fig. 4a that the influence of Na on nitrous oxide formation is rather complex. First, on addition of sodium the temperature window over which N<sub>2</sub>O is formed shifts towards lower temperatures. This is related to the shift in

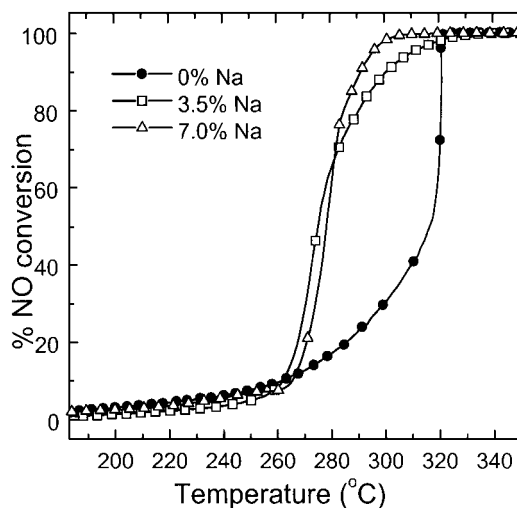
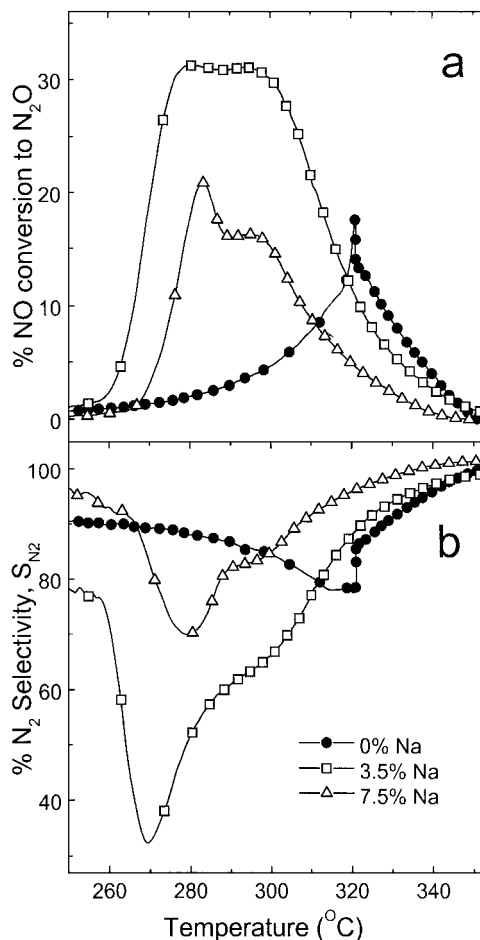


FIG. 3. The influence of sodium content on light-off performance for NO reduction to all products (N<sub>2</sub> and N<sub>2</sub>O).  $S=1$ , [NO]=1000 ppm, [C<sub>3</sub>H<sub>6</sub>]=1067 ppm, [CO]=7000 ppm, [O<sub>2</sub>]=7800 ppm,  $W/F=0.015$  g s cm<sup>-3</sup>.



**FIG. 4.** The effect of sodium content on N<sub>2</sub>O and N<sub>2</sub> formation as a function of temperature: (a) %NO conversion to nitrous oxide, and (b) %N<sub>2</sub> selectivity,  $S_{N_2}$ , defined as  $[N_2]/([N_2] + [N_2O]) \times 100/1$ .  $S = 1$ ,  $[NO] = 1000$  ppm,  $[C_3H_6] = 1067$  ppm,  $[CO] = 7000$  ppm,  $[O_2] = 7800$  ppm,  $W/F = 0.015$  g s cm<sup>-3</sup>.

NO conversion temperature as depicted in Fig. 3. Second, addition of sodium up to 3.5 wt% Na significantly increases the total formation of N<sub>2</sub>O, by broadening the temperature window and increasing the value of the peak maximum, from 15% over the unpromoted catalyst to 31% for 3.5 wt% Na. On increasing the sodium loading further, however, the opposite trend is observed; i.e., the temperature window narrows and the value of the peak maximum decreases, to approximately 20% at 7.0 wt% Na.

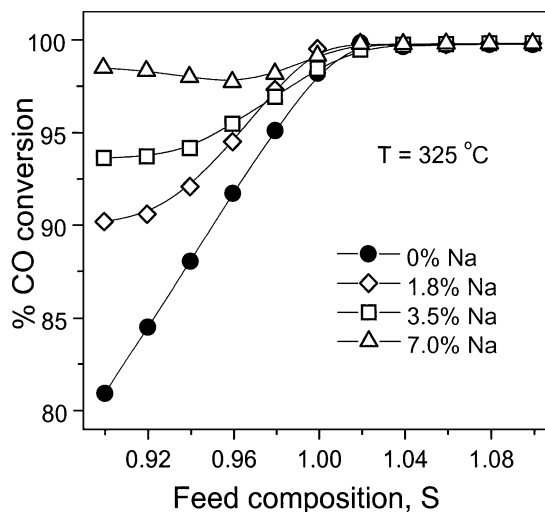
The corresponding selectivity data are shown in Fig. 4b. Initially, at low NO conversion, the selectivity towards N<sub>2</sub> is high for each catalyst. However, as the temperature increases the selectivity drops to a minimum and then increases again to 100% at temperatures above ~360°C. Addition of 3.5 wt% Na significantly decreases the value of the selectivity minimum from ~80% over the unpromoted catalyst to ~40%. However, further addition of sodium brings the minimum back up to ~73% at 7.0 wt% Na loading.

### 3.3. Influence of Sodium on Conversions as a Function of $S$

In order to investigate the influence of sodium under both oxidising and reducing conditions, “ $S$  sweep” experiments were performed by varying the oxygen concentration between 6970 ppm ( $S = 0.90$ ) and 8630 ppm ( $S = 1.10$ ) whilst maintaining the bed temperature fixed at 325°C ( $[NO] = 1000$  ppm,  $[CO] = 7000$  ppm,  $[C_3H_6] = 1067$  ppm,  $W/F = 0.015$  g s cm<sup>-3</sup>).

The influence of sodium loading on CO conversion as a function of feed composition is depicted in Fig. 5. At  $S \geq 1$  (oxygen rich), the CO conversion under these conditions is 100% on all the catalysts tested. However, as oxygen is removed from the feed stream,  $S < 1$ , the CO conversion over the unpromoted catalysts drops steadily to approximately 81% at  $S = 0.90$ . It is clear from this figure that the addition of sodium helps to maintain high levels of CO conversion, to such an extent that for the 7.0 wt% Na-loaded sample the CO conversion remains above 97% even at  $S = 0.90$ . As the reactant feed is oxygen deficient under these conditions, this improvement in CO oxidation must be accompanied by a decrease in C<sub>3</sub>H<sub>6</sub> conversion, as shown in Fig. 6. In this case the propene conversion over the unpromoted catalyst is above 95% at  $S = 0.90$ . However, as sodium is added there is a systematic decrease in hydrocarbon conversion at  $S \leq 1$ , such that for the 7.0 wt% Na catalyst the C<sub>3</sub>H<sub>6</sub> conversion has decreased to ~84% at  $S = 0.90$ .

The corresponding data for NO conversion are displayed in Fig. 7. In this case there is a significant decrease in NO conversion under oxygen-rich conditions ( $S > 1.00$ ), from 100% at  $S = 1.00$  to ~50% at  $S = 1.10$  over the unpromoted catalyst. In this region of the  $S$  sweep the addition of sodium is not beneficial to total NO reduction; indeed there is a



**FIG. 5.** The influence of sodium loading on CO conversion as a function of feed composition,  $S$ .  $T = 325^\circ\text{C}$ ,  $[NO] = 1000$  ppm,  $[C_3H_6] = 1067$  ppm,  $[CO] = 7000$  ppm,  $[O_2]$  varied between 6970 and 8630 ppm,  $W/F = 0.015$  g s cm<sup>-3</sup>.

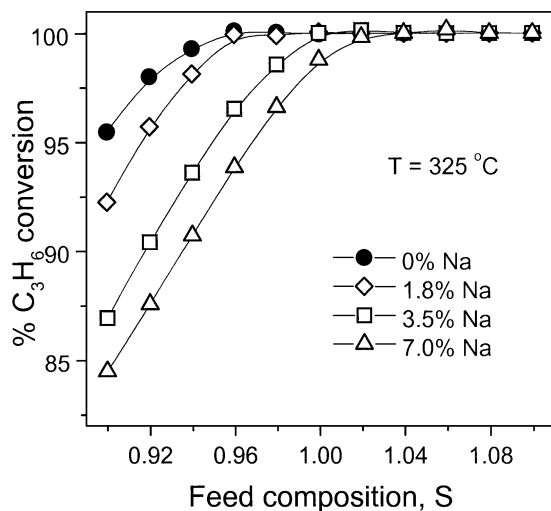


FIG. 6. The influence of sodium loading on  $C_3H_6$  oxidation as a function of feed composition,  $S$ .  $T = 325^\circ C$ ,  $[NO] = 1000$  ppm,  $[C_3H_6] = 1067$  ppm,  $[CO] = 7000$  ppm,  $[O_2]$  varied between 6970 and 8630 ppm,  $W/F = 0.015$  g s  $cm^{-3}$ .

small but significant decrease in NO conversion over the sodium-loaded samples.

Under fuel-rich conditions ( $S < 1.00$ ), however, the presence of sodium does improve NO conversion (Fig. 7). Over the unpromoted catalysts there is a significant decrease in NO conversion as  $S$  decreases, to below 90% at  $S = 0.90$ . This decrease is more apparent in the inset to Fig. 7, which shows an extension of the fuel-rich region down to  $S = 0.60$  ( $[O_2] = 4480$  ppm), in which the NO conversion is seen to decrease to values as low as 30%. Although this observation may appear surprising, it is a well-known feature of palladium catalysts and has been attributed in previous stud-

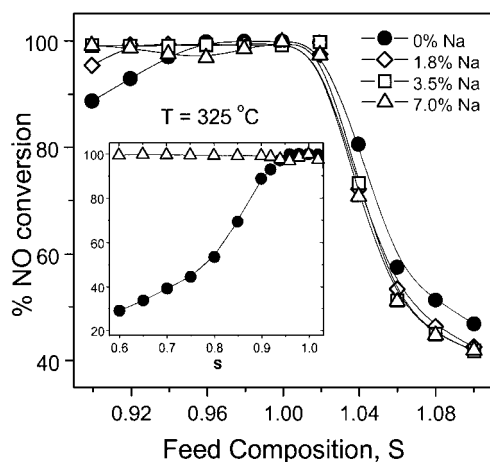


FIG. 7. The influence of sodium loading on NO conversion to all products as a function of feed composition,  $S$ .  $T = 325^\circ C$ ,  $[NO] = 1000$  ppm,  $[C_3H_6] = 1067$  ppm,  $[CO] = 7000$  ppm,  $[O_2]$  varied between 6970 and 8630 ppm,  $W/F = 0.015$  g s  $cm^{-3}$ .

ies to coke or carbonaceous deposits on the metal surface (3, 5). It is clear that under these oxygen-deficient conditions the presence of sodium is strongly beneficial, helping to maintain NO conversions close to 100% at  $S = 0.60$  for the 7.0 wt% Na sample.

### 3.4. Influence of Sodium on Nitrogen Selectivity as a Function of $S$

The formation of nitrous oxide as a function of feed composition is shown in Fig. 8a. It is interesting to note that at the temperature employed ( $325^\circ C$ ), the minimum in  $N_2O$  formation occurs at the stoichiometric point ( $S = 1.00$ ), with excursions into both fuel-rich and oxygen-rich regimes significantly increasing the production of this undesirable species, although the increase is much more pronounced in the  $O_2$ -rich region. For each catalyst the maximum in  $N_2O$  formation occurs at approximately  $S = 1.04$ , with a value of  $\sim 45\%$  NO conversion to  $N_2O$  for the unpromoted catalyst. The decrease in  $N_2O$  production above  $S = 1.04$  is related to the overall decrease in NO conversion. It is apparent that in both oxygen-rich and fuel-rich regions the presence of sodium significantly reduces the production  $N_2O$ . For the

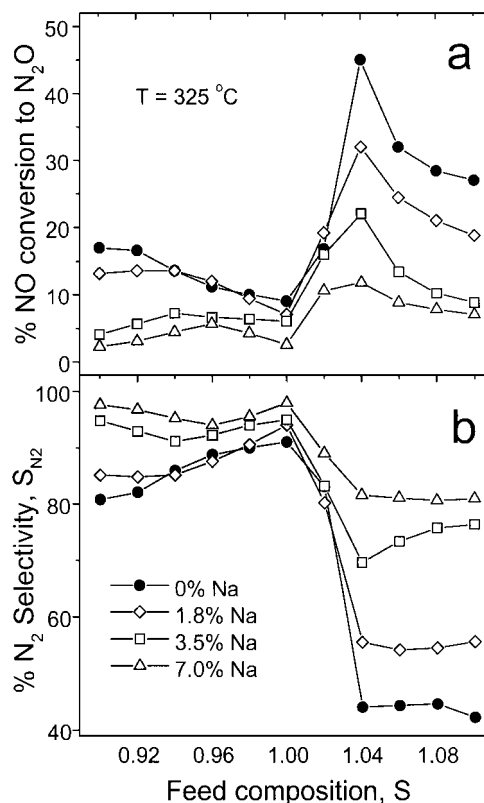


FIG. 8. The influence of sodium loading on (a) nitrous oxide formation and (b) nitrogen selectivity (%) as a function of feed composition,  $S$ .  $T = 325^\circ C$ ,  $[NO] = 1000$  ppm,  $[C_3H_6] = 1067$  ppm,  $[CO] = 7000$  ppm,  $[O_2]$  varied between 6970 and 8630 ppm,  $W/F = 0.015$  g s  $cm^{-3}$ .

7.0 wt% Na catalyst the production of  $N_2O$  never exceeds  $\sim 10\%$  over the entire range of feed compositions investigated.

The corresponding  $\%N_2$  selectivity is plotted in Fig. 8b (defined as  $\%S_{N_2} = [N_2]/([N_2] + [N_2O]) \times 100/1$ ). In the oxygen-rich region the selectivity declines very substantially to only  $\sim 45\%$  over the unpromoted catalyst for values of  $S = 1.04$  or above. However, the addition of sodium systematically improves the selectivity, until at 7.0 wt% Na loading the selectivity is maintained above 80% in the  $O_2$ -rich region. Improvements in selectivity are also observed in the fuel-rich region although again the effects are not as pronounced. The nitrogen selectivity decreases to  $\sim 80\%$  over unpromoted catalyst at  $S = 0.90$ , whilst it is maintained at over 95% for the 7.0 wt% Na sample.

#### 4. DISCUSSION

Before discussing the mechanism of alkali promotion in detail, it is worth recalling the principal effects observed on addition of sodium to these catalysts:

- (i) enhanced activity for CO and  $C_3H_6$  oxidation at  $S = 1$  (lower  $T_{50}$ );
- (ii) enhanced activity for NO reduction at  $S = 1$  (lower  $T_{50}$ );
- (iii) improved NO reduction under fuel-rich conditions (reduced hydrocarbon poisoning);
- (iv) enhanced selectivity towards  $N_2$  as opposed to  $N_2O$  under both rich and lean conditions.

We may rationalise these observations in terms of the effects of Na on the adsorption strength and (in the case of NO) dissociation behaviour of the reactants. On the basis of our earlier kinetic and spectroscopic results for the electrochemical promotion by Na of NO reduction by CO (11) and by propene (12) over Pt catalysts, we proposed an explanation for the mechanism of Na promotion. This mechanism for promotion by Na and the supporting theoretical (20) and experimental (21) evidence have been described and discussed in detail previously (12). We propose that adsorbed Na acts to (i) increase the adsorption strength of electronegative adsorbates (CO, NO,  $O_2$ ) at the expense of electropositive adsorbates ( $C_3H_6$ ) and (ii) weaken the N–O bond in the adsorbed molecule which therefore facilitates NO dissociation.

These effects are due to the influence of the electrostatic field of the alkali cation on adjacent coadsorbed molecules. For example, in the case of NO, coadsorbed alkali acts to lower the NO  $\pi^*$  antibonding orbital energy below the Fermi energy, thus populating the former with valence electrons from the metal. This results in strengthening of the metal–N bond and weakening of the N–O bond, enhancing NO adsorption and promoting its dissociation. Our

conclusions are in accord with the FTIR studies of Liotta *et al.* (22), who studied CO adsorption on sodium-promoted Pd/SiO<sub>2</sub> catalysts. They observed a systematic shift towards lower frequency for all the carbonyl bands on increasing the sodium content of their catalysts, which they attributed to a decrease in the C–O bond order due to increased back donation of electron density from Pd d orbitals to the antibonding  $\pi^*$  orbitals of the coordinated carbonyls.

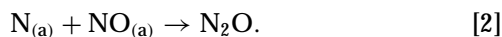
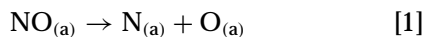
The improved light-off performance over sodium-promoted catalysts (Figs. 1–3) may therefore be explained as follows. The strong adsorption of propene and its dissociation fragments on the unpromoted metal surface reduces the number of available active sites. By promoting adsorption of electronegative species, particularly the oxidants NO and  $O_2$ , alkali acts to reduce this self-poisoning effect, modifying the relative coverage of each species such that the various oxidation/reduction reactions can proceed more favourably.

This effect also accounts for the substantial improvement in NO conversion under reducing conditions observed on addition of sodium to the samples (Fig. 7). Here again, self-poisoning by hydrocarbon is significantly diminished, allowing the 7.0 wt% Na sample to maintain 100% NO conversion at  $S = 0.60$ . However, under oxidising conditions ( $S > 1$ ) no promotional effect of sodium on NO conversion is observed. Here NO and  $O_2$  must compete for the available reduced sites on the metal surface. As both are electronegative species the influence of sodium on their *relative* coverages is small. Indeed, it appears that sodium may actually slightly favour  $O_2$  adsorption under these conditions, accounting for the small decrease in NO conversion observed over the Na-containing samples at values of  $S = 1.04$  or above.

Alkali-promoted adsorption of electronegative species (CO, NO,  $O_2$ ) relative to propene and its decomposition products is also apparent when we consider the influence of sodium on CO and  $C_3H_6$  conversions under reducing conditions (Figs. 5 and 6, respectively). Under these conditions ( $S < 1.00$ ) CO and  $C_3H_6$  must compete for the available oxidant. On the unpromoted catalysts, conversion of propene is favoured relative to CO (95% and 81%, respectively, at  $S = 0.90$ ). However, as sodium is added to the samples we observe a systematic decrease in  $C_3H_6$  conversion (to 84% for 7.0 wt% Na at  $S = 0.90$ ), accompanied by a corresponding increase in CO conversion (to 98% for 7.0 wt% Na at  $S = 0.90$ ), which once again signifies promoted adsorption of the electronegative species (CO in this case) relative to  $C_3H_6$ .

We now consider the influence of sodium on nitrous oxide production. The formation of  $N_2O$  is highly undesirable as it is a strong greenhouse gas and also contributes to stratospheric ozone depletion (23). The formation of this species is generally agreed (12, and references therein) to proceed

via the following steps:



With the formation of  $\text{N}_2$  occurring via combination of two adsorbed nitrogen atoms,



The formation of  $\text{N}_2\text{O}$  is therefore maximised at an optimum ratio of  $\text{N}_{(a)}$  to  $\text{NO}_{(a)}$  surface coverage and can be limited by either low initial NO coverage and/or very fast (or slow) rates of NO dissociation. NO dissociation on palladium is known to be strongly structure sensitive, being favoured by stepped sites (24, 25). Single-crystal studies have also shown that NO dissociation varies strongly as a function of NO coverage (26), being favoured at low coverages where lateral adsorbate interactions do not interfere with further dissociation. It is also important to note that the rate of NO dissociation increases significantly with temperature (27, 28), which accounts for the observed 100%  $\text{N}_2$  selectivity at temperatures above  $\sim 350^\circ\text{C}$  in Fig. 4.

The influence of Na loading on  $\text{N}_2\text{O}$  production under stoichiometric conditions, where the formation of  $\text{N}_2\text{O}$  is observed to first increase and then decrease with Na loading (Fig. 4a), may be explained as follows. On the one hand, by shifting the NO light-off (Fig. 3) towards lower temperatures (where the dissociation rate is lower), and increasing the relative coverage of NO (vs  $\text{C}_3\text{H}_6$ ), the addition of sodium tends to favour  $\text{N}_2\text{O}$  production. However, this effect is counteracted by the influence of coadsorbed alkali on the population of the NO  $\pi^*$  antibonding orbitals as discussed above. This acts in the opposite manner and tends to increase NO dissociation resulting in a decrease in  $\text{N}_2\text{O}$  production (Na may also activate new sites for NO dissociation as discussed below). It is the interplay between these opposing effects which accounts for the complex behaviour observed. Therefore, although both 3.5 and 7.0 wt% Na samples have similar light-off temperatures, the catalyst with higher sodium content is more selective towards nitrogen.

Before discussing the influence of sodium content on  $\text{N}_2\text{O}$  production under both oxidising and reducing conditions, as shown in Fig. 8a, we must first account for the trends observed over the unpromoted catalyst. At  $S=1$  the formation of  $\text{N}_2\text{O}$  is low under these conditions due to the relatively high temperature employed ( $325^\circ\text{C}$ , cf. Fig. 4a), which results in high rates of NO dissociation. However, as the  $\text{O}_2$  content in the stream is increased up to  $S=1.04$ , the production of  $\text{N}_2\text{O}$  is seen to increase significantly, which can be attributed to the increased coverage of  $\text{O}_{(a)}$  interfering with NO dissociation (26) (increasing  $\theta_{\text{NO}}$  and shifting the  $\theta_{\text{N}}/\theta_{\text{NO}}$  ratio towards values more favourable for  $\text{N}_2\text{O}$  formation). At values of  $S > 1.04$ , the production of

$\text{N}_2\text{O}$  decreases due to decreased NO coverage caused by the competition between  $\text{O}_2$  and NO for reduced sites, which will tend to favour oxygen as its gas-phase concentration increases. Therefore, the  $\text{N}_2\text{O}$  maximum at  $S=1.04$  in Fig. 8a is bounded on the left-hand side by a region ( $1.00 < S < 1.04$ ) in which the high rate of NO dissociation is limiting, and on the right-hand side by a region ( $S > 1.04$ ) in which the coverage of NO is limiting.

The systematic decrease in  $\text{N}_2\text{O}$  formation (Fig. 8a), and corresponding increase in  $S_{\text{N}_2}$  (Fig. 8b), with sodium loading under these oxygen-rich conditions must therefore be due to sodium maintaining high levels of NO dissociation in the presence of increasing  $\text{O}_{(a)}$  coverages. A possible explanation for this may be that sodium activates previously inactive low-index planes on palladium for the dissociative adsorption of NO, therefore greatly increasing the number of active sites available. This greater number of sites would subsequently be able to accommodate higher oxygen coverages whilst retaining relatively high rates of NO dissociation. Sodium activation of previously inactive low-index planes has previously been proposed to account for the dramatic increase in activity on addition of Na to Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts tested for the NO +  $\text{C}_3\text{H}_6$  reaction (14, 15).

A similar argument can be applied to the increase in  $\text{N}_2\text{O}$  production under fuel-rich conditions ( $S < 1$ ) over the unpromoted catalyst (Fig. 8a), which in this case can be attributed to blocking of sites required for NO dissociation by  $\text{C}_3\text{H}_6$  or derived fragments. However, it is clear that oxygen is much more effective at blocking the palladium sites required for NO dissociation than hydrocarbon fragments.

In summary therefore, we have shown that addition of sodium to Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst significantly improves both their activity and  $\text{N}_2$  selectivity under simulated three-way conditions over a range of stoichiometry from fuel rich to fuel lean. The optimum loading for the catalysts studied in this work was found to be 7.0 wt% Na as this was the maximum loading (giving the highest  $\text{N}_2$  selectivity) that could be achieved without overextensive active site blocking.

The observed behaviour is understandable in terms of the electronic effect of Na on coadsorbates. Alkali promotes the adsorption of electronegative species (oxygen, NO) (21, 29) and weakens the adsorption of electropositive species (propene) (30). This effectively "cleans off" the metal surface and increases the overall oxidation activity of both oxygen and NO. Sodium also strongly promotes NO dissociation under both oxidising and reducing conditions, therefore significantly increasing the nitrogen selectivity.

## CONCLUSIONS

1. Sodium promotion yields large improvements in the performance of Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts in the conversion of

NO, CO, and propene in simulated exhaust gas under stoichiometric conditions.

2. Under fuel-rich conditions, hydrocarbon poisoning of NO reduction is completely suppressed in the presence of Na.

3. Sodium significantly reduces the formation of N<sub>2</sub>O under both reducing and oxidising conditions.

4. Promotion is due to the effects of sodium on the relative adsorption strengths and (in the case of NO) dissociation behaviour of the reactants.

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